

Kinetic study on photocatalytic degradation of reactive orange 5 solution with phosphotungstic acid

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Abstract

Increasing environmental pollution caused by toxic dyes due to their hazardous nature is a matter of great concern. It has been generally agreed that reactive orange 5 (KGN) can be effectively degraded in aerated phosphotungstic acid (HPA) homogeneous reaction system using near-UV irradiation. The knowledge on the kinetics of the system possesses both practical and theoretical value. The results reveal that the photocatalytic degradation reaction of KGN with HPA in a homogenous solution can be described by Langmuir–Hinshelwood equation; the results manifest the reaction is first-order with lower concentration and is zero-order with higher concentration. As the initial concentration goes up, the order of the reaction is reduced from 1 to 0, the limiting rate constant and the adsorption constant in this case are $0.8098 \text{ mg L}^{-1} \text{ min}^{-1}$ and $4.359 \times 10^{-2} \text{ L mg}^{-1}$, respectively. The paper reveals that the optimal amount of photocatalyst in our experimental conditions for the degradation of KGN is 0.6 g L^{-1} . The effects of irradiation intensity and pH value on the degradation rate constant were also demonstrated, where special attention was paid on the nature of the photocatalyst itself.

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1. Introduction

Increasing environmental pollution caused by toxic dyes due to their hazardous nature is a matter of great concern [1]. Azo dyes, the largest class of synthetic dyes used in food industries, are characterized by the presence of one or more azo bonds ($-\text{N}=\text{N}-$) in association with one or more aromatic systems, which may also carry sulfonic acid groups. Many studies indicate that these dyes are toxic or carcinogenic. Moreover, these dyes cannot be removed by conventional wastewater treatment systems nowadays [2,3]. Therefore, the employment of these dyes must be controlled and the effluents must be treated before being released into the aquatic and terrestrial environment [4].

There are several methods used to decolorize the textile wastewater, but they cannot be effectively applied for all dyes [5]. Activated carbon adsorption process for the removal of dyes is an accepted practice, but the cost of treatment is high. Ozone

and hypochlorite oxidations are effective decolorization methods, but they are not desirable because of the high cost of the equipments, operating costs and the secondary pollution arising from the residual chlorine [6].

Therefore, the interest in developing processes which can destroy these dyes effectively has been a hot issue recently. Photocatalysis by solid polyoxometalate (POM) is a new branch in the field of photocatalytic chemistry, and some attractive researching progresses have developed in recent years. POMs exhibit UV light photocatalytic activity in homogeneous system [7]. Mechanistic aspects of photocatalysis by these non-toxic compounds are well known. In fact, many of POMs share very similar photochemical characteristics of the semiconductor photocatalysts, and POMs represent the analogues of semiconductor metal oxides [8,9]. The photochemical behavior of POMs has been studied extensively in homogeneous systems [9–17]. However, kinetic studies on their photooxidative behavior have received less attention compared with the semiconductor photocatalysts.

Reactive orange 5 (KGN) is a water-soluble azo dye, which is widely applied in tanning and textile industries. Thus, in the present paper, KGN was chosen as the model azo dye.

Abbreviations: KGN, reactive orange 5; HPA, phosphotungstic acid; L–H, Langmuir–Hinshelwood; POM, polyoxometalate.

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Nomenclature

C_0	initial concentration of KGN (mg L^{-1})
C_t	concentration of KGN at moment t (mg L^{-1})
t	reaction time (min)
K_{obs}	the observed pseudo first-order rate constant (min^{-1})
k_0	observed zero-order rate constant ($\text{mg L}^{-1} \text{min}^{-1}$)
k	L–H rate constant ($\text{mg L}^{-1} \text{min}^{-1}$)
K	Langmuir adsorption constant (L mg^{-1})

In this paper, kinetic study on photocatalytic degradation of KGN with phosphotungstic acid (HPA) was investigated and the initial reaction rate and its relating factors were emphasized. Efforts were paid to draw conclusions on the apparent kinetic model, effects of initial concentration, intensity of light and amount of catalyst.

2. Experimental

2.1. Materials and instruments

HPA, was of analytical grade, was purchased from Chemtech Kelong Chemical Reagents Factory and used as received. Reactive orange 5 was donated by Dalian University of Technology.

A Shimadzu UV-120-02 spectrophotometer, an HY-4 vibrator and a 20 W medical ultraviolet lamp (Philips, with maximum emission at 254 nm) were used in the experiments. Water used in the experiments was deionized and fully aerated by the vibrator.

2.2. Procedures

A quartz tube (1.5 cm diameter, 100 cm length) was used as the reactor. A 100 mL KGN solution containing 60 mg HPA was introduced into the reactor each time in the dark room. Then the mixture was fixed on the vibrator and was put under the UV illumination at the distance of 15 cm while being stirred continuously to keep it uniform. Samples were withdrawn at specific time intervals. Changes in the concentration of KGN were measured by the spectrophotometer at 485 nm.

The degradation was carried out at room temperature and pH 2.0. The pH value was adjusted with HClO_4 (0.1 mol L^{-1}) and sodium hydroxide (0.1 mol L^{-1}) solution and monitored by a pH-meter when necessary. The structure of KGN is shown in Fig. 1.

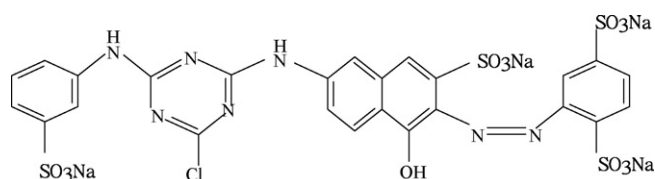


Fig. 1. structure of reactive orange 5.

3. Results and discussion

3.1. Blank experiments

The contrast experiments were carried out in two conditions: one with HPA but no illumination, the other with illumination but no catalyst. The results showed that the concentration of KGN solution (10 mg L^{-1}) kept the same under the former condition, while in the later case changed so little that could be ignored (during 90 min time period). The blank tests proved the stability of KGN. Without illumination or photocatalysts, KGN is kinetically stable.

3.2. Kinetics on the destruction of KGN

In general, for TiO_2 heterogeneous reaction system, the kinetics would follow the Langmuir–Hinshelwood (L–H) model [18–21]. Mylonas and Papadimitrakou [22] and Turchi and Ollis [23] reported that the kinetics also follow the L–H model for homogeneous reaction system.

$$r = \frac{dC}{dt} = \frac{kKC_t}{1 + KC_t} \quad (1)$$

where r is photocatalytic degradation rate; k is L–H rate constant; K is the Langmuir adsorption constant of the KGN in the photocatalytic degradation reaction; and C_t is the concentration of the KGN under study.

Figs. 2 and 3 show information on the kinetic of photocatalytic degradation for eight various concentrations under identical conditions.

Fig. 2 is a plot of normalized concentrations versus irradiation time for KGN at three high initial concentrations ($\geq 100 \text{ mg L}^{-1}$), it is clear that C_t versus t is in linear form, which shows that the degradation rates fit a zero-order model well, that is the $C_t = C_0 - k_0t$ describes the tendency well, where C_0 and C_t are the concentration of KGN at time 0 and t , respectively, and k_0 is the observed zero-order rate constant. Fig. 3 is a plot of normalized concentrations versus irradiation time for KGN at five low initial concentrations ($\leq 30 \text{ mg L}^{-1}$). The logarithmic trans-

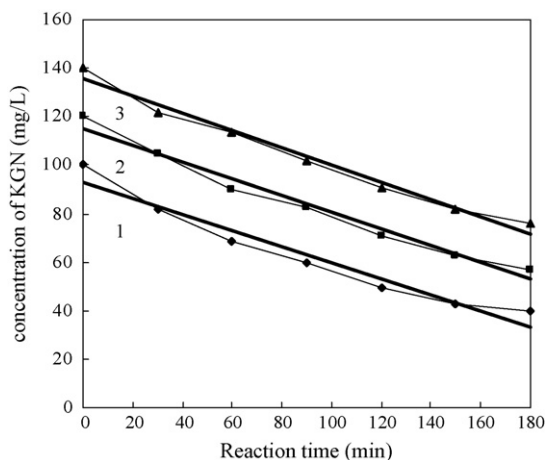


Fig. 2. Plot of photo-degradation of KGN versus irradiation time at various initial concentrations of KGN: (1) 100 mg L^{-1} , (2) 120 mg L^{-1} and (3) 140 mg L^{-1} .

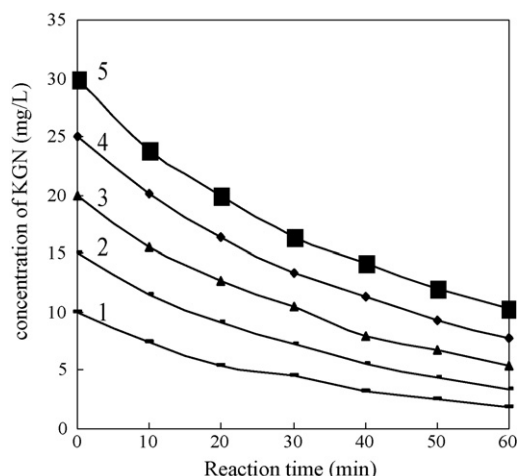


Fig. 3. Plot of photo-degradation of KGN versus irradiation time, at various initial concentrations of KGN: (1) 10 mg L⁻¹, (2) 15 mg L⁻¹, (3) 20 mg L⁻¹, (4) 25 mg L⁻¹ and (5) 30 mg L⁻¹.

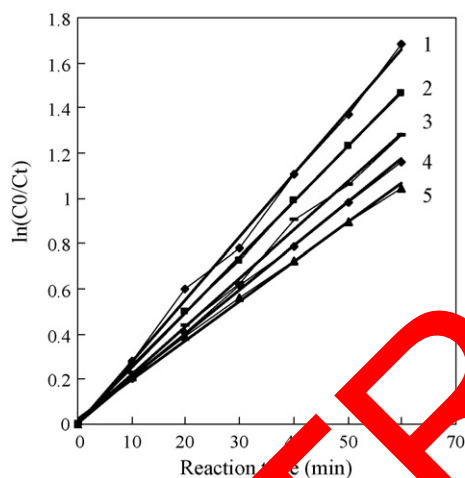


Fig. 4. $\ln(C_0/C_t)$ versus illumination time. Initial concentration of KGN: (1) 10 mg L⁻¹, (2) 15 mg L⁻¹, (3) 20 mg L⁻¹, (4) 25 mg L⁻¹ and (5) 30 mg L⁻¹.

forms for these concentration curves are shown in Fig. 4. The degradation rates fit the first-order model well, that is, the integral equation of $\ln(C_0/C_t) = K_{\text{obs}}t$ describes the tendency well, where C_0 and C_t are the concentration of KGN at time 0 and t , respectively, and K_{obs} is the observed pseudo first-order rate constant. The slope of a linear plot of $\ln(C_0/C_t)$ versus time gives the apparent degradation rate constant. To make the further mathematic inferences clear, all the relating kinetic parameters, such as the

Table 1
Parameter and reaction kinetic equation for different initial concentration

C_0 (mg L ⁻¹)	Reaction kinetic equation	Rate constant	$t_{0.5}$ (min)	R
10	$\ln(C_0/C_t) = 0.0276t + 0.0032$	0.0276 min ⁻¹	25.00	0.9889
15	$\ln(C_0/C_t) = 0.0244t + 0.0077$	0.0244 min ⁻¹	28.09	0.9998
20	$\ln(C_0/C_t) = 0.0213t + 0.0088$	0.0213 min ⁻¹	32.13	0.9990
25	$\ln(C_0/C_t) = 0.0194t + 0.0120$	0.0194 min ⁻¹	35.11	0.9997
30	$\ln(C_0/C_t) = 0.0173t + 0.0273$	0.0173 min ⁻¹	38.49	0.9990
100	$C_t = 91.777 - 0.3221t$	0.3221 mg L ⁻¹ min ⁻¹	142.47	0.9875
120	$C_t = 112.64 - 0.3271t$	0.3271 mg L ⁻¹ min ⁻¹	172.18	0.9954
140	$C_t = 132.35 - 0.3301t$	0.3301 mg L ⁻¹ min ⁻¹	200.47	0.9980

Table 2
Relating kinetic parameters on the photo-degradation of KGN

C_0 (mg L ⁻¹)	$1/C_0$ (L mg ⁻¹)	r_0 (mg L ⁻¹ min ⁻¹)	$1/r_0$ (L min mg ⁻¹)
10	0.10	0.2451	4.0800
15	0.0667	0.3333	3.0000
20	0.0500	0.3745	2.6702
25	0.0400	0.4081	2.4504
30	0.0333	0.4717	2.1200

reaction rate constants (K_{obs}), half-life ($t_{0.5}$) and interrelated coefficients (R) of the lines in Fig. 3 and Fig. 4, are all presented in Table 1. It is clear that the rate constant is inversely proportional to the initial concentration of KGN to the lowest limit of 30 mg L⁻¹. The decrease of K_{obs} as increasing the initial KGN concentration indicates that there is a competition between the instantaneous intermediates and KGN for the oxidant [20]. In the process of degradation, the higher initial concentration is, the more intermediates appear and the stronger negative effects on the apparent reaction rate constant. As to the negative effect of initial concentration, it can be speculated to be caused by the limited dosage of oxidants which is fixed in our case because the intermediates would compete with KGN for oxidant. Considering the results above, the oxidation reaction is probably the rate-determining step.

The further information of r_0 (the initial rate) of the five low initial concentrations (≤ 30 mg L⁻¹) was shown in Table 2.

Owing to the complex mechanism of reactions, it is difficult to develop a model for the dependence of the photocatalytic degradation rate on the experimental parameters for the whole treatment time. Thus, kinetic modeling of the photocatalytic process is usually restricted to the analysis of the initial rate of photocatalytic degradation. This can be obtained from the initial slope to the curves and the initial concentration in an experiment in which the variation of the concentration is measured as a function of time. The extrapolation of the photocatalytic degradation rate to time = 0 avoids the possible interference from by-products. The initial photocatalytic degradation rate (r_0) is observed to be a function of the initial concentration (C_0). A linear plot of r_0^{-1} versus C_0^{-1} is often obtained, and that gives k as the L-H rate constant and K as the Langmuir adsorption constant of the KGN in the photocatalytic degradation reaction [19,20].

$$r_0 = \frac{kKC_0}{1 + KC_0} \quad (2)$$

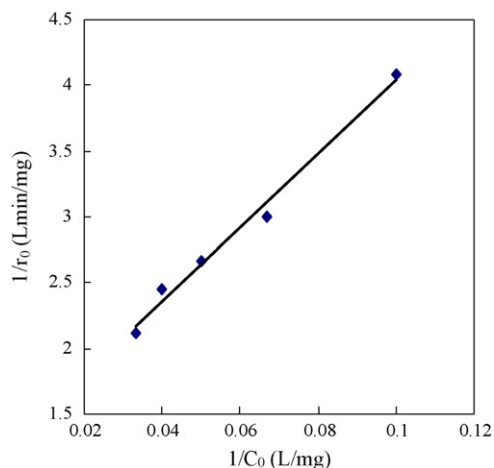


Fig. 5. The linear transformation of $1/r_0$ versus $1/C_0$.

The equation is further expressed in a linear form:

$$\frac{1}{r_0} = \frac{1}{kKC_0} + \frac{1}{k} \quad (3)$$

In order to find the effect of initial concentration on the photocatalytic degradation and half-life, more detailed analysis was fulfilled based on the kinetics of photocatalytic degradation. Fig. 5 shows plot of the reciprocal of the initial rate r_0^{-1} versus the reciprocal of the initial concentration C_0^{-1} for photocatalytic degradation of KGN. The kinetic parameters k and K were obtained using linear least squares analysis. The value of k and K are $0.8098 \text{ mg L}^{-1} \text{ min}^{-1}$ and $4.359 \times 10^{-5} \text{ L mg}^{-1}$, respectively. By substituting the k and K values into Eq. (3), the analytical relationship between r_0 and C_0 is obtained. It is clear that a good fitting of the model to the experimental data may be observed thus confirming the L–H nature of the photocatalytic degradation reaction mechanism.

Actually, L–H kinetic model has successfully described many similar homogeneous photocatalytic systems [24,25].

3.3. Effect of irradiation intensity

Irradiation intensity from the irradiation source is an important factor in photocatalytic reaction. In order to find the effect of irradiation intensity of UV light on the photocatalytic degradation kinetics, varying the distance (13.7, 25.2, 35.3, 45.5 and 56.0 cm) between the surface of the UV lamp and the quartz tube controlled the irradiation intensity of UV light. When the concentration of KGN solution (10 mg L^{-1}) and other conditions were fixed, the effect of irradiation intensity on the kinetics was shown in Fig. 6.

The kinetic reaction rate constants were obtained using linear least squares analysis. Relating kinetic parameters were shown in Table 3.

As shown in Table 3, it was found that the photocatalytic kinetics depends on the irradiation intensity. When irradiation intensity is below $1001 \times$, the reaction is zero-order, while when irradiation intensity is above $1001 \times$, the reaction is first-order. The tendency of the effect by irradiation intensity was similar to

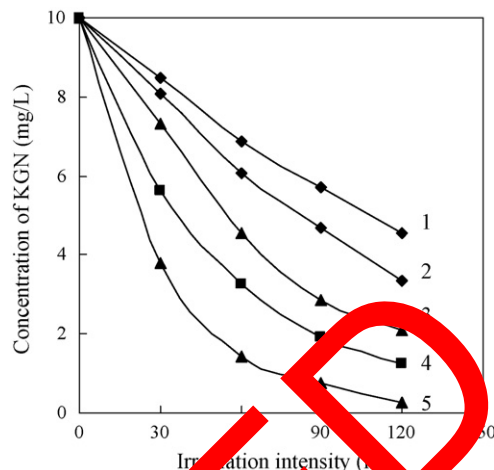


Fig. 6. The effect of irradiation intensity on the photocatalytic degradation of KGN, irradiation intensities (1) $54.31 \times$, (2) $73.81 \times$, (3) $1071 \times$, (4) $1491 \times$ and (5) $3331 \times$.

Table 3
Effect of irradiation intensity on photocatalytic kinetics

Distance (cm)	Irradiation intensity (lx)	Kinetic equation	R
13.7	33.3	$\ln(C_0/C_t) = 0.0302t + 0.0585$	0.9973
25.2	14.9	$\ln(C_0/C_t) = 0.0176t + 0.0519$	0.9981
35.3	7.1	$\ln(C_0/C_t) = 0.0144t + 0.0289$	0.9989
45.5	73.8	$C_t = 9.815 - 0.056t$	0.9944
56.0	54.3	$C_t = 10.017 - 0.0473t$	0.9953

the previous results [1,26]. From above result, it is reasonable to speculate that for low concentration solution of dyes the reaction is zero-order when irradiation intensity is low, while the reaction is first-order when irradiation intensity is high.

To further investigate the effect of irradiation intensity on the first-order reaction rate constants, the data in Table 3 was analyzed using linear least squares analysis and the result was shown in Fig. 7. The K versus irradiation intensity is in good linear form, the equation is $y = 6.974 \times 10^{-5}x + 7.092 \times 10^{-3}$

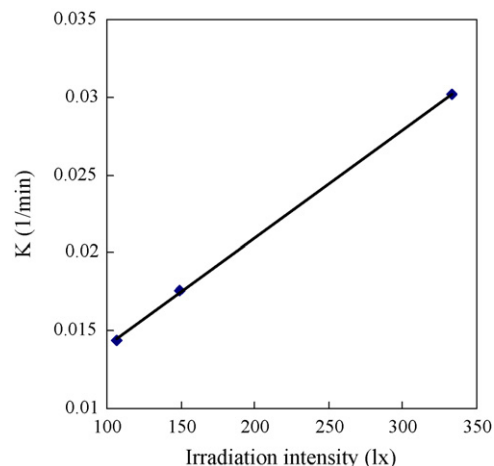


Fig. 7. Relationship between the irradiation intensity and the reaction rate constant.

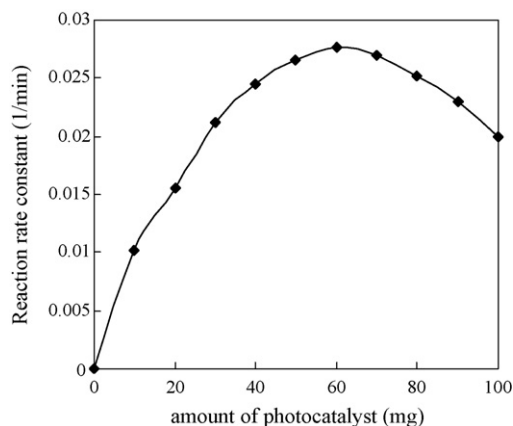


Fig. 8. Effect of catalyst amount on reaction rate constant.

($R=0.9998$). From the results above, irradiation intensity takes an important role in photocatalytic reaction. More attentions should be focused on the influence of irradiation intensity on the reaction kinetics.

3.4. Effect of the amount of the photocatalyst

The initial concentration of the KGN solution was 10 mg L^{-1} . The effect of amount of photocatalyst on the apparent reaction rate constant was shown in Fig. 8. The result indicates that the optimal amount of catalyst in our case is around 0.6 g L^{-1} . Since more catalysts lead to more effective oxidants, the photo-degradation efficiency increases with the dosage of catalyst at first; then the curve drops sharply at 0.7 g L^{-1} due to the effect of the amount of photocatalyst on photocatalytic degradation, it is interesting that there is a maximum amount of HPA, but it is not clear to explain why the apparent reaction rate constant drops dramatically upon further addition of the catalyst. A similar phenomenon has also been reported and discussed by some researchers in dealing with dyes using TiO₂ as photocatalysts [27–30]. The similar phenomenon was observed when we dealt with other dyes using HPA as photocatalysts. Hu and Xu [27] ascribed this result to the fact that HPA has a limited solubility in water, but we think this explanation is not convincing under our experimental condition because 100 mg HPA can be completely dissolved in 100 mL water. Einaga [31] reported the photocatalytic degradation rate of 4-chlorophenol with HPA was proportional to the catalyst concentration in the optically dilute region and when the catalyst concentration higher than 0.7 mM , the rate was saturated due to the complete light absorption by catalyst. However, our result is not the same as that of Einaga, so more detailed study needs to be further investigated in the near future.

Considering the results here and above, to increase the dosage of the catalyst blindly is not an effective way to enhance the degradation efficiency.

3.5. Effect of pH on the reaction rate constant of KGN

pH value can be one of the most important parameters for the photocatalytic process and so it has long been of a focus

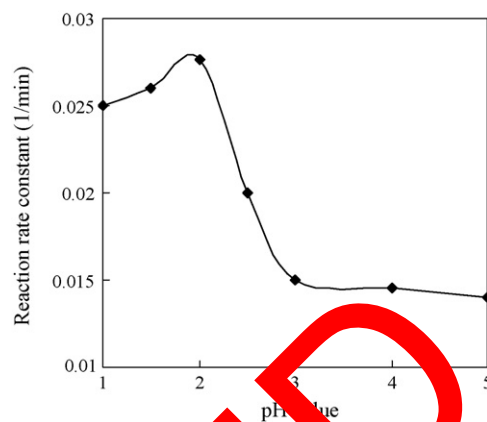


Fig. 9. Effect of pH value on the reaction rate constant.

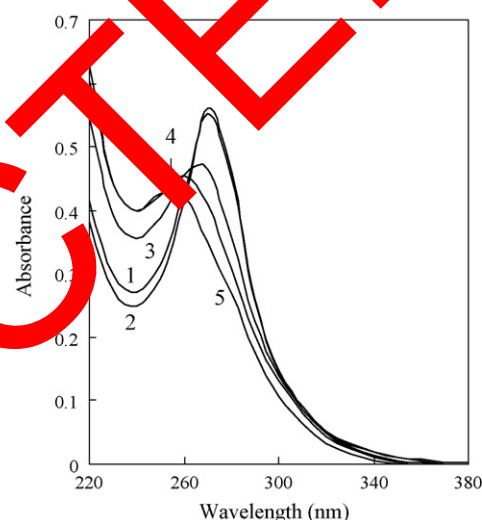


Fig. 10. UV spectrum of phosphotungstic acid in aqueous solution.

to study its influence on the degradation rate constant. When the concentration of KGN solution (10 mg L^{-1}) and other optimum conditions were fixed, the pH value of the mixed solution was adjusted continuously by HClO_4 (0.1 mol L^{-1}) and sodium hydroxide (0.1 mol L^{-1}) solution. Fig. 9 shows the variation of apparent reaction rate constant as a function of pH value. The reaction rate constant increases with the pH value at first; then the curve drops sharply when pH is above 2, while there is a maximum value at about pH 2. The UV spectrum of phosphotungstic acid in aqueous solution has a blue-shifted with the increasing of the pH value (Fig. 10), which clearly shows that the structure of HPA has been changed. When pH 2.5, 26.8% HPA was degraded into $\text{H}_7\text{PW}_{11}\text{O}_{39}$, which decreases the photocatalytic activity, thus the reaction rate constant is low [31]. So more attentions should be focused on the nature of photocatalyst itself.

4. Conclusions

The paper reveals that the optimal amount of photocatalyst in our experimental conditions for the degradation of KGN is 0.6 g L^{-1} . It is also demonstrated that the degradation is

a pseudo first-order reaction when the concentration of KGN is below 30 mg L^{-1} and the degradation is zero-order reaction when the concentration of KGN is above 100 mg L^{-1} , and Langmuir–Hinshelwood kinetic model describes it well. Mathematical inference show that the limiting rate constant and the adsorption constant in this case are $0.8098 \text{ mg L}^{-1} \text{ min}^{-1}$ and $4.359 \times 10^{-2} \text{ L mg}^{-1}$, respectively. The effects of irradiation intensity and high pH value on the degradation rate were also demonstrated, where special attention was paid on the nature of the photocatalyst itself.

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